

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 March 2001 (01.03.2001)

PCT

(10) International Publication Number
WO 01/15258 A1

(51) International Patent Classification⁷: H01M 10/40,
8/10, 6/16, H01B 1/20, 1/22, H01G 9/025, 9/028

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(21) International Application Number: PCT/IB00/01286

(22) International Filing Date: 23 August 2000 (23.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PQ 2371 23 August 1999 (23.08.1999) AU

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AT
(utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA,
CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility
model), DK, DK (utility model), DM, DZ, EE, EE (utility
model), ES, FI, FI (utility model), GB, GD, GE, GH, GM,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK
(utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*



WO 01/15258 A1

(54) Title: ION CONDUCTIVE MATERIAL HAVING A DOPANT ION IN AN ORGANIC MATRIX PHASE

(57) Abstract: This invention relates to ion conducting materials which are prepared by doping conductive ions into a crystalline matrix. Such materials have particular application in batteries as electrolytes. Broadly, the invention relates to a solid state conductive material including a dopant ion, which is the substantially conductive species, in an organic matrix phase. The organic matrix phase includes a cation which may be selected from one or more of the ammonium cations, the pyrrolidinium cations, the imidazolium cations, the pyrrolidinium cations, morpholinium cations and/or cations containing a positively charged phosphorous, and a weak base anion, forming an organic salt. The dopant is preferably included at a concentration between 1 and 49 % by weight of the overall material. The preferred dopant is Li⁺ and the preferred materials are lithium ion conductive electrolytes.

ION CONDUCTIVE MATERIAL HAVING A DOPANT ION IN AN ORGANIC MATRIX PHASEFIELD OF INVENTION

5 This invention relates to ion conductive materials which find application in electrochemical devices as electrolytes. Such devices include batteries, capacitors, photoelectrochemical solar cells, electrochromic devices and sensors. In particular the invention relates to solid state lithium ion conductive electrolytes for lithium battery applications.

10

BACKGROUND TO THE INVENTION

Lithium ion conductors are of significance because of the role that they play in the lithium battery. Concern about the safety and stability of solvent based
15 electrolytes has necessitated the use of lithium intercalation materials as anodes, at the cost of additional mass and volume. Solid state lithium ion conductors would produce a more stable lithium anode and present fewer safety issues(1). Thus attention has focused on solid-state lithium ion conductors, including glasses, ceramics and polymers. The first two of these conduct by a fast ion
20 conduction mechanism, in which the lithium ion moves within an essentially static framework. The polymer systems resemble solvent based electrolytes in that the motions of the ions are mediated by the motions of the polymer. This, in the absence of any other component in the form of a low molecular weight solvent, restricts the conductivity to relatively low values and the lithium ion
25 contributes only a small fraction of the conductivity(2). It has been shown (3) that this produces severe concentration gradients during cell operation, causing premature failure. Higher conductivities can be produced by the inclusion of large amounts of low molecular weight solvents, forming what are known as "gel" electrolytes. These, however, still possess undesirable solvent volatility
30 and flammability problems.

A substance in which one of the ionic species is able to conduct much more rapidly, often by a factor of many orders of magnitude, than any other species

present is referred to as a fast ion conductor. A typical example is the Li^+ ion in the ceramic material $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (4,5). At room temperature the ions involved in the structure of this material are essentially immobile, in the sense of long range diffusive and conductive motions. In contrast, the Li^+ ions exhibit conductivity as high as 10^{-3} S/cm at room temperature. The occurrence of this decoupling of the motion of one ion from the motions of others has been of fundamental interest for many years. Models of fast ion conduction in ceramics consider the motion to be along interconnected tunnels in the solid lattice and/or to involve ion hopping between empty sites in the lattice. While the single crystal conductivity of these materials can be high, the polycrystalline nature of the bulk material creates grain boundaries which lower the overall conductivity to levels unsuitable for electrochemical devices.

Plastic crystalline substances have also been known for many years (6) and those based on ionic species can exhibit ion conduction (7 - 15). The crystalline state of these substances is typically fully ordered at low temperatures. However, as the temperature is increased one or more first order solid-solid phase transitions are observed. In these higher temperature phases there exists some degree of rotational disorder; eg. in Li_2SO_4 (13-15) the SO_4^{2-} anion is free to rotate in the fcc phase of this compound above 575°C , but is nonetheless fixed on its lattice site. Ikeda et al (8-11) and Cooper and Angell (12) have studied organic ion plastic crystals and observed most to exhibit some level of intrinsic conductivity. This is understood to be associated with the rotational motions of one or more of the ions and also of the lattice defects created. Cooper and Angell (12) prepared "double salt" compounds that showed plastic crystal behaviour and had conductivities as high as 4×10^{-6} S/cm at 25°C , the bulk of which was attributed to Li^+ ion motion. Such levels of conductivity are too low to be of interest in most electrochemical applications.

Solid electrolytes are also extremely desirous in other electrochemical applications, including, for example, those listed below.

- (i) Low temperature fuel cells. These typical require a proton conducting material and the lack of a sufficiently high proton

conductivity under various operating conditions is currently a limitation on this type of fuel cell.

- (ii) Photoelectrochemical cells. In these cells the electrolyte is desirably non-volatile and solid in order that it can be easily and conveniently sealed into the device. The species required to be conductive depends on the details of the cell construction. One of the favoured designs involves an electrolyte which is able to transport iodide and iodine species.
- (iii) Electrochromic devices. These devices have a number of types of differing electrochemistry, but all preferably require a solid electrolyte of low volatility.
- (iv) Capacitors - electrolytic and electrochemical (double layer) types. These devices rely on electrolytes to conduct charge between the electrodes. In both types lifetime is limited under some operational circumstances by volatilization of the electrolyte and therefore low volatility electrolytes are desirous. The provision of solid electrolytes in such devices may also enable volume savings in the device.
- It is an object of the present invention to provide a new class of ion conducting materials which reduces or overcomes at least some of the abovementioned disadvantages, or which at least provides the public with a useful alternative. Other objects of the invention may become apparent from the following description, given by way of example.

SUMMARY OF THE INVENTION

According to one aspect of the present invention there is provided a solid state conductive material including a dopant ion, which is the substantially conductive species, in an organic matrix phase.

Preferably, the organic matrix phase includes a cation and an anion forming an organic salt.

Preferably, the cation may include one or more cations containing a positively charged nitrogen and/or positively charged phosphorus.

Preferably, the anion may comprise a weak base anion.

5

Preferably, the dopant ion may be Li^+ .

Preferably, the dopant concentration may be between 0.01% and 90% of the overall material by weight, more preferably between 1 and 49% of the overall material by weight.

10

The invention also relates to the use of these solid state conductive materials as an electrolyte in an electrochemical device, and to such electrochemical devices including, as an electrolyte, these solid state conductive materials.

15

Other aspects of the present invention may become apparent from the following description which is given by way of example only and with reference to the accompanying examples.

20 DETAILED DESCRIPTION OF THE INVENTION

In the materials reported here, ion conductive phases are obtained by doping a compound containing the desired conductive ion into organic crystalline phases. The organic salt acts as a solid state solvent or "matrix" for the dopant ions.

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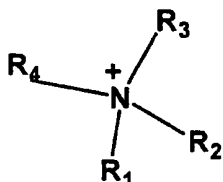
Thus for example, lithium ion conductive phases are obtained by doping a lithium compound into organic crystalline phases. The organic salt acts as a solid state solvent or "matrix" for the Li ions.

30 Whilst the invention is described with specific reference to doping with lithium, it will be appreciated that this invention has application to other conductive ions, such as, for example, protons, Na^+ , Mg^{2+} , Al^{3+} , Ag^+ , Cl^- , I^- , etc.

The crystalline phases which can serve as useful matrix phases in this invention preferably involve a cation and an anion forming an organic salt. The cation is comprised of one or more of the cations selected from:

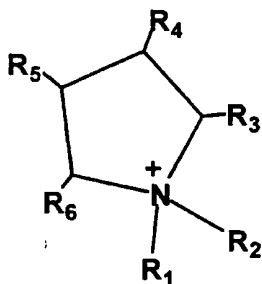
- (i) the ammonium cations

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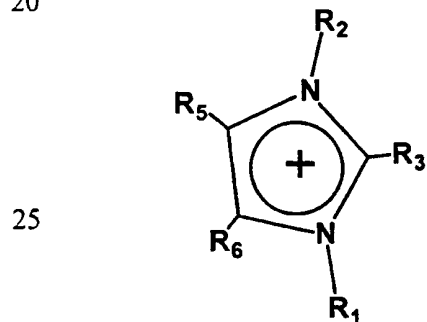
- 10 (ii) the pyrrolidinium cations

15



- (iii) the imidazolium cations

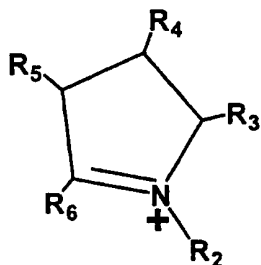
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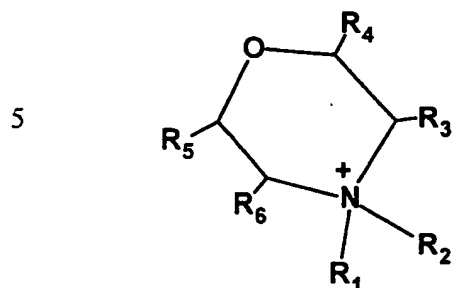
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- (iv) the pyrrolidenium cations

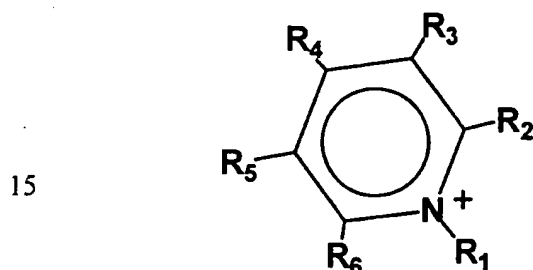
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(v) the morpholinium family of cations



10 (vi) pyridinium cations



(vii) guanadinium family of cations

20 (viii) other cations containing a positively charged nitrogen

(ix) cations containing a positively charged phosphorous.

25 In each of these structures R1, R2, R3, R4, R5, R6 can be H, methyl, ethyl, propyl, butyl, s-butyl, pentyl, hexyl or any alkyl group in general, which may also be branched. The chain may also contain hetero-atoms, a halogen, a nitrile group, and generally other groups or ring fragments consistent with the substituent promoting or supporting rotatory motions of the species in the solid state.

30

The anion associated with these cations can be one or more of the following:

(i) BF_4^-

(ii) PF_6^-

- (iii) CH_3SO_3^- or CF_3SO_3^-
- (iv) $(\text{CH}_3\text{SO}_2)_2\text{N}^-$ or $(\text{CF}_3\text{SO}_2)_2\text{N}^-$
- (v) CF_3COO^-
- (v) other sulfonyl compounds
- 5 (vi) cyanide and dicyanamide
- (vii) succinimide and perfluorinated succinimide
- (viii) ethylenedisulfonylamide and its perfluorinated analogue
- (ix) SCN^-
- (xi) other carboxylic acid derivatives
- 10 (xii) other weak base anions
- (xiii) halide ions such as the iodide ion.

Some of these salts may form plastic crystal phases which enhance the conduction process.

15

Either the cation or the anion may be part of a polymer chain. Such polymers include the following polycation: the polyvinylpyridinium cation, polyvinylpyrrolidinium cation, the polyethyleneimine cation and copolymers of these with other polymerizable monomers. Polyanions include, polymers or
20 copolymers containing the triflylimide pendant group and the sulphonic acid pendant group, as well as fluorinated analogues of these.

Alternatively the compound may be of a plastic crystal forming habit but not itself ionic. In this variation, all that is required is that the organic matrix or
25 "solvent phase" in this case be of a sufficiently polar nature that it can act as a solvent for the dopant conducting ion. Such compounds include for example alcohols.

The dopant ion containing salt which is mixed with the matrix crystal phase may
30 contain one or more ions in common with the matrix phase, in which case the doping can be considered as a single ion substitution, or it may involve entirely different ions. In the lithium dopant ion case the dopant salt may be a lithium salt of the same anion as the matrix or may be a lithium salt of another anion for

example those in the above list of anions. In the case where the desired dopant species is a proton, the dopant species may be an acid.

5 The dopant concentration can be between 0.01% and 90% of the overall material by weight. Preferably the dopant concentration is between 1 and 49% by weight of the overall material.

10 Doping is achieved by mixing the dopant salt into the molten state of the matrix compound and then cooling the material into its plastic crystalline state. The result is a waxy solid material at room temperature in the cases of some members of the above salt families. Alternatively the finely powdered materials may simply be mixed and pressed together, to form a coherent material. Elevated temperatures accelerate the process of interdiffusion. It is also possible to prepare the materials by codissolution in a common solvent followed by
15 removal of the solvent under vacuum.

In the case of the lithium doped materials, doping with less than 1 cation% Li^+ produces a 20-fold increase in conductivity at 25°C in comparison with undoped, pure matrix phase. The conductivity continues to increase up to
20 50mol% Li(bistrifluoromethanesulfonyl)imide (otherwise known as lithium imide). Beyond this point the conductivity falls; pure lithium imide is practically non-conductive. Whereas at low concentrations only one phase is observed and Li^+ can be considered to be a dopant in the matrix phase, at higher Li^+ concentrations we observed a eutectic at 30°C indicating the presence of two
25 phases in the samples. Comparison with a lithium imide based polymer electrolyte (17) indicates that the plastic crystal materials of the present invention are as conductive as analogous solid polymer electrolytes, but at substantially lower lithium ion concentrations. On a gravimetric basis the highest conductivity in the polymer electrolyte case is reached beyond 1 mol/kg
30 at 25°C (17), whereas equivalent conductivity is reached in the plastic crystal materials at less than 0.1 mol/kg.

- Some light is shed on the complexity of the conductivity behaviour by thermal analysis. The thermograms show a number of solid-solid phase transitions that are present in some of the pure host and doped materials. As discussed elsewhere in respect of the pure host (16, 7-11), some of these phase transitions, the first of which takes place at -90°C, correspond to the onset of rotational motion of one or more parts of the molecules involved. Whether it is the cation or the anion in the matrix phase that is responsible for the rotational disorder is not yet conclusively known. The melting transition of the doped compound is broadened and slightly shifted compared to the pure compound. In addition, no new thermal transitions, eg. eutectic melting, are observed, indicating that the material probably represents a solid solution of the dopant in the parent structure. In this case where a eutectic mixture forms, it is to be expected that above the eutectic temperature the material will exhibit conduction due to both the fast-ion conduction of the crystalline phase but also liquid state conduction due to both ions of the matrix phase. This can produce a higher conductivity but such conductivity may be due to motion of undesirable ions. Hence for some applications the most preferred region of compositions and temperature is that where single ion conduction is observed.
- At still higher salt concentrations, it is possible that the mixture forms new mixed salt compounds as observed by Cooper and Angell in their study of double salts (12).
- The materials of the invention can be classified as fast ion conductors on the basis of the high conductivities observed in a crystalline lattice. Many of these crystalline materials have plastic mechanical properties at room temperature, ie., at some value of applied stress the materials will yield and exhibit plastic flow.
- Representative examples of the ion conducting materials of the invention, and their method of manufacture, are now described with specific reference to lithium doped materials.

Example 1

A mixture of 2% by mol Lithium bis(trifluoromethanesulfonyl)amide is mixed with methylethylpyrrolidinium bis(trifluoromethanesulfonyl)amide by melting the two compounds together (melting point around 90°C). Cooling the material to
5 around room temperature produces a waxy material of conductivity around 0.01mS/cm at room temperature.

The mixture prepared in this example was melted and impregnated in its molten state into a separator that is used in the preparation of a standard button cell type
10 lithium battery.

Example 2

Methylpropylpyrrolidinium hexafluorophosphate is prepared and mixed with 5 mol% lithium hexafluorophosphate by melting the two compounds together.
15 Cooling the material to room temperature produces a waxy material which has conductivity around 0.2mS/cm.

Example 3

Methylpropylpyrrolidinium tetrafluoroborate is prepared and mixed with 5
20 mol% lithium tetrafluoroborate by melting the two compounds together. Cooling the material to room temperature produces a waxy material which has conductivity above 0.1mS/cm.

Example 4

Methylpropylpyrrolidinium dicyanamide is prepared and mixed with 5 mol% lithium triflate by melting the two compounds together. Cooling the material to
25 room temperature produces a waxy material which has conductivity above 0.1mS/cm.

Example 5

A mixture of 2% by mol Lithium bis(trifluoromethanesulfonyl)amide is mixed with methylmorpholinium bis(trifluoromethanesulfonyl)amide by melting the two compounds together. Cooling the material to around room temperature produces a waxy material of conductivity around 0.1mS/cm at room temperature.

Example 6

A mixture of 5% by mol Lithium bis(trifluoromethanesulfonyl)amide is mixed with dimethylimidazolium bis(trifluoromethanesulfonyl)amide by melting the two compounds together. Cooling the material to around room temperature produces a waxy material of conductivity around 0.01 mS/cm at room temperature.

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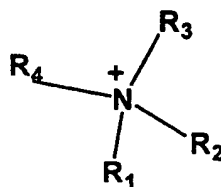
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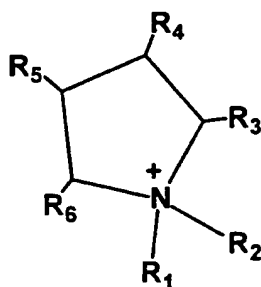
CLAIMS

1. A solid state conductive material including a dopant ion, which is the substantially conductive species, in an organic matrix phase.
2. A solid state conductive material according to claim 1 wherein the organic matrix phase includes a cation and anion forming an organic salt.
3. A solid state conductive material according to claim 2 wherein the cation includes one or more cations containing a positively charged nitrogen and/or positively charged phosphorous.
4. A solid state conductive material according to claim 3 wherein the cation includes one or more of:

- an ammonium cation



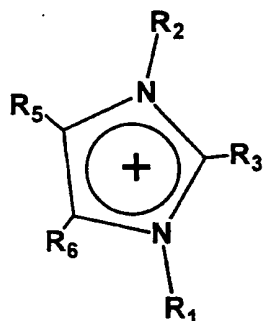
- a pyrrolidinium cation



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- an imidazolium cation

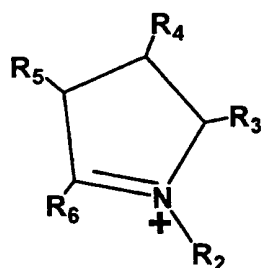
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- a pyrrolidenium cation

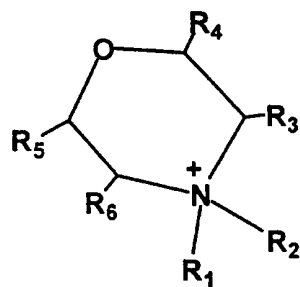
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- a morpholinium cation

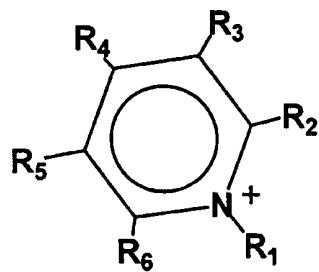
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- a pyridinium cation

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- a guanadinium cation

5 wherein the or each of R1, R2, R3, R4, R5 and R6 are selected from any substituent or substituents promoting or supporting rotary motion of the species in a solid state.

10 5. A solid state conductive material according to claim 4 wherein the or each of R1, R2, R3, R4, R5 and R6 are selected from H and any substituted or unsubstituted, branched or straight-chain alkyl group, with or without one or more heteroatoms in the chain.

15 6. A solid state conductive material according to any one of claims 2 to 5 wherein the anion is a weak base anion.

7. A solid state conductive material according to any one of claims 1 to 6 wherein the dopant ion is Li^+ .

20 8. A solid state conductive material according to claim 7 wherein the dopant concentration is between 0.01% and 90% of the overall material by weight.

25 9. A solid state conductive material according to claim 8 wherein the dopant concentration is between 1 and 49% of the overall material by weight.

30 10. A solid state conductive material including Li^+ ions as a conductive species in an organic matrix phase, formed from an integral mixture of methylpropylpyrrolidinium hexafluorophosphate with 5 mol% lithium hexafluorophosphate.

11. A solid state conductive material according to any one of claims 1 to 10 when used as an electrolyte in an electrochemical device.

12. An electrochemical device including as an electrolyte a solid state
conductive material according to any one of claims 1 to 10.
13. A solid state conductive material substantially as herein described and
with reference to any one of the accompanying examples.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB00/01286

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : H01M 10/40, 8/10, 6/16, H01B 1/20, 1/22, H01G 9/025, 9/028		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl. ⁷ : H01M 10/40, 8/10, 6/16, H01B 1/20, 1/22, H01G 9/025, 9/028		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI, JAPIO, IFIPAT: Int.Cl. as above with li, lithium, ion?, salt, pyrrolidinium, ammonium, imidazolium, pyrrolidinium, morpholinium, pyridinium, guanadinium		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 281994 A (NIPPON CHEMI-CON CORPORATION) 14 September 1988 Page 3, lines 47 - 52	1 - 9, 11
X	EP 822608 A (SAMSUNG ELECTRONICS CO., LTD.) 4 February 1998 Whole document	1-2, 6-9, 11
X	US 5091274 A (HSIUE et al.) 25 February 1992 Abstract	1,11
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Date of the actual completion of the international search 29 November 2000		Date of mailing of the international search report 4 - DEC 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer RAJEEV DESHMUKH Telephone No : (02) 6283 2145

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB00/01286

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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T	MACFARLANE et al., "Lithium-doped plastic crystal electrolytes exhibiting fast ion conduction for secondary batteries", Nature, Vol. 402, 16 December 1999, pages 792-794	
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Information on patent family members

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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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